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## Laboratory Determination of Signature Criteria for Locating and Monitoring Abandoned Mine Fires

By Ann G. Kim

UNITED STATES DEPARTMENT OF THE INTERIOR



BUREAU OF MINES



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**UNITED STATES DEPARTMENT OF THE INTERIOR**  
Manuel Lujan, Jr., Secretary

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## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	angstrom	g	gram
Btu	British thermal unit	h	hour
Btu/lb	British thermal unit per pound	in	inch
Btu/scf	British thermal unit per standard cubic foot	kcal/mol	kilocalorie per mole
°C	degree Celsius	kg	kilogram
cfcd	cubic foot per day	lb	pound
cm <sup>3</sup> /g	cubic centimeter per gram	pct	percent
ft	foot	ppm	part per million
ft <sup>3</sup>	cubic foot	scfh	standard cubic foot per hour

# LABORATORY DETERMINATION OF SIGNATURE CRITERIA FOR LOCATING AND MONITORING ABANDONED MINE FIRES

By Ann G. Kim<sup>1</sup>

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## ABSTRACT

The U.S. Bureau of Mines mine fire diagnostic methodology to locate and monitor fires in abandoned mines and waste banks is based on the controlled sampling of the mine atmosphere to determine changes in the concentration of hydrocarbons desorbed from heated coal. To provide background data for this methodology, a laboratory study was conducted in which samples of coal and coal waste were heated under controlled conditions. Gas samples from the combustion furnace were analyzed for standard gases CO<sub>2</sub> and CO and for the C<sub>1</sub> to C<sub>5</sub> hydrocarbons. In all tests, the concentration of desorbed hydrocarbons increased during heating and decreased during cooling. A dimensionless hydrocarbon ratio, R1, was developed as the signature for heated coal. For bituminous coals, the value of R1 increases during heating of coal samples and decreases during cooling of the same samples. Generally, R1 values of 100 or more indicate coal sample temperatures of at least 100° C. The emission of higher molecular weight hydrocarbons from anthracite samples was very low, resulting in relatively low R1 values at all temperatures. Data from field projects confirmed these results.

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## INTRODUCTION

Fires in abandoned mines and waste banks are a relatively common occurrence in coal-producing areas. A survey in the 1970's by the U.S. Bureau of Mines identified 292 waste bank fires and 261 fires in abandoned mines (9, 24).<sup>2</sup> Fires occur in every coal-producing State (table 1). Abandoned mine fires present a serious health, safety, and environmental hazard, due to emission of toxic fumes, subsidence, and deterioration in air quality. Such fires usually depress property values for affected land and adjacent areas. Although there are several fire extinguishment methods, the cost of controlling an abandoned mined land fire is usually high and the success rate is often low (4).

**Table 1.—Abandoned mined land fires in waste banks and underground mines (9, 24)**

State	Waste banks	Mines
Alabama . . . . .	6	NR
Alaska . . . . .	NR	3
Arizona . . . . .	NR	10
Colorado . . . . .	15	47
Illinois . . . . .	4	NR
Kentucky . . . . .	27	5
Maryland . . . . .	2	2
Montana . . . . .	3	65
New Mexico . . . . .	NR	9
North Dakota . . . . .	NR	15
Ohio . . . . .	6	7
Oklahoma . . . . .	1	NR
Pennsylvania . . . . .	74	42
South Dakota . . . . .	NR	2
Texas . . . . .	NR	1
Utah . . . . .	4	17
Virginia . . . . .	17	NR
Washington . . . . .	1	2
West Virginia . . . . .	132	8
Wyoming . . . . .	NR	26
Total . . . . .	292	261

NR None reported.

In almost all cases, the application of any fire control method is made more difficult by the inability to accurately locate the fire. A fire in an abandoned underground mine or waste bank is usually detected because smoke is emitted along an outcrop or through natural vents or fractures. Because hot gases follow the path of least resistance, surface evidence of venting gases may not occur directly above subsurface fire zones. Likewise, aerial infrared photography can detect only heated surface areas. Attempts to extrapolate surface data to underground locations require that heated gases migrate along straight-line paths, a condition that is usually not met. Interpretation

of aerial infrared can also be complicated by the presence of heat-absorbing surface features.

Determining subsurface temperatures through boreholes can provide more information; however, the results are highly variable. Generally, thermocouples measure the highest temperature within a volume of 1 to 2 ft<sup>3</sup> immediately surrounding the thermocouple tip. Because abandoned coal mine fires are usually smoldering combustion, because they tend to be discontinuous, and because surrounding rock can serve as an insulating medium, it is possible to measure near-normal underground temperatures within several feet of a combustion zone. Experience with methods that depend on measurable changes in a physical parameter, such as temperature, has shown them to lack accuracy and sensitivity.

Indicators based on the evolution of products of combustion, such as the Jones-Trickett ratio (5, 10), the air-free ratio of CO<sub>2</sub> to CO (22), and the submicrometer particle detector (23), often give ambiguous results when applied to abandoned mine fires. These indicators depend on measurable changes related to combustion. In an abandoned mine, only a small fraction of the coal and carbonaceous material may be involved in smoldering combustion. Also, CO<sub>2</sub> may be produced and oxygen maybe consumed by processes other than combustion, such as bacterial metabolism and ambient temperature oxidation. If the concentration of oxygen is greater than 17 pct, errors in calculated air-free ratios and in oxygen deficiency ratios tend to become very large, even when measurement error is relatively small. The dilution factor, the length of the ventilation pathway, and the relative sampling volume may also be factors in the low accuracy of product-of-combustion indicators when used at abandoned mines.

In conjunction with its work on innovative methods of controlling abandoned underground mine and waste bank fires (2-3), the Bureau is developing a mine fire diagnostic methodology to accurately determine the location and extent of underground abandoned mine fires and to establish measurable criteria for determining when such fires are extinguished (15). The methodology involves determining borehole temperatures and pressures and gas compositions under two conditions: natural and when a pressure gradient is imposed. Overcoming the natural ventilation pathways forces gases desorbed from heated coal to migrate in controlled directions. An integral part of the mine fire diagnostic methodology is the determination of a signature value based on the temperature-dependent desorption of low-molecular-weight hydrocarbons from heated coal. The purpose of this laboratory study is to develop a data base relating hydrocarbon desorption from various coals to temperature. These results are correlated with data obtained at several mine fire sites.

<sup>2</sup>Italic numbers in parentheses refer to items in the list of references at the end of this report.



This project was funded under the Abandoned Mined Land research program administered by the U.S. Office of Surface Mining Reclamation and Enforcement (OSMRE) under Interagency Agreement HQ-51-CT6-01535 (15). Field work at Carbondale, PA, was performed under

Interagency Agreement CT745011 with the Wilkes-Barre, PA, office of OSMRE. Work at Large, PA, was done under a Memorandum of Agreement with the Pennsylvania Department of Environmental Resources.

## HYDROCARBON SIGNATURE CRITERIA

The emission of methane ( $\text{CH}_4$ ) and other hydrocarbon gases from coal is a well-known phenomenon. Changes in methane emission rate and the emission of other hydrocarbons at elevated temperatures are a function of the internal structure of the coal and the concentration of adsorbed gases (14). The internal structure of coal is like a sponge with many small interconnected pores (micropores) with an average diameter of 5 to 20 Å (21). Coal also has a system of cracks or fractures (macropores), which intersect the micropore system. Both the fracture density and the width of the fractures can vary (20). The hydrocarbon gas formed during coalification is contained in both the micropore and macropore systems. This gas is a mixture of methane, ethane, propane, isobutane, isopentane, and normal butane and pentane (table 2) (13, 18-19). The gas in coal may also contain small amounts of  $\text{CO}_2$  and hydrogen, which are products of coalification; oxygen and nitrogen, which are occluded during deposition or introduced by percolating ground water; and helium, which is a product of radioactive decay. Normally, coalbed gas is more than 90 pct hydrocarbons. Elevated concentrations of  $\text{CO}_2$  are frequently associated with areas of tectonic activity. CO and sulfur compounds are not normally found in gas removed from coalbeds. Based on their boiling points (table 2), all of the low-molecular-weight hydrocarbons associated with coal would be in the gaseous state at normal ground temperatures. The heats of adsorption (table 2) indicate that these hydrocarbons would be readily adsorbed and desorbed at the temperatures and pressures normally associated with coalbeds. The hydrocarbons in coal can therefore be assumed to exist both as free gas in the pores and fractures and adsorbed on the internal surface of the coal. Under all temperature and pressure conditions, some of the gas is emitted from the coal. The emission of the gas involves several steps, each of which is dependent on several factors. Within the micropore, gas is adsorbed and desorbed at some rate dependent upon the concentration of the gas, the pressure, and the temperature. Under stable conditions, an equilibrium exists and the amounts of desorbed gas and adsorbed gas remain relatively constant. Apparently, most of the desorbed gas is methane, probably because more methane is formed during coalification and because less energy is required to desorb the lighter methane molecule. Eventually, a gas molecule leaves the

micropore, by diffusion, and enters the macropore system (fig. 1). Movement of gas molecules through the fractures within the solid coal is thought to follow Darcy's law (laminar flow), the rate being dependent on the fracture permeability, the variation in pressure, and the dynamic gas viscosity (1). The rate at which gas is emitted from the coal to the atmosphere is dependent upon temperature, the pressure differential between the coal and the atmosphere, the rank of the coal, the degree of fracturing, the permeability of the coal, and the permeability of adjacent strata.

Table 2.—Components of coalbed gas

Component	Molecular formula	Molecular weight	Boiling point, °C	Heat of adsorption, <sup>1</sup> kcal/mol
Hydrocarbons:				
Methane . . . . .	$\text{CH}_4$	16	-164	3.1
Ethylene . . . . .	$\text{C}_2\text{H}_4$	28	-103.7	4.4
Ethane . . . . .	$\text{C}_2\text{H}_6$	30	-88.6	4.4
Propylene . . . . .	$\text{C}_3\text{H}_6$	42	-47.4	5.9
Propane . . . . .	$\text{C}_3\text{H}_8$	44	-42.1	6.0
Isobutane . . . . .	i- $\text{C}_4\text{H}_{10}$	58	-12.0	6.9
Butane . . . . .	n- $\text{C}_4\text{H}_{10}$	58	9.5	7.5
Neopentane . . . . .	neo- $\text{C}_5\text{H}_{12}$	72	9.5	6.9
Isopentane . . . . .	i- $\text{C}_5\text{H}_{12}$	72	27.9	8.0
Pentane . . . . .	n- $\text{C}_5\text{H}_{12}$	72	36.1	8.5
Other gases:				
Hydrogen . . . . .	$\text{H}_2$	2	-252.8	Nap
Helium . . . . .	He	4	-268.9	Nap
Nitrogen . . . . .	$\text{N}_2$	28	-198.5	Nap
Carbon monoxide <sup>2</sup> . . . . .	CO	28	-191.5	Nap
Oxygen . . . . .	$\text{O}_2$	32	-182.9	Nap
Carbon dioxide . . . . .	$\text{CO}_2$	44	-78.5	Nap

Nap Not applicable.

<sup>1</sup>On carbon black. Average of values determined by di Corci (7), Hoory (8), Kalasnikova (12), and Ross (25).

<sup>2</sup>CO is not normally found in gas desorbed from coal. It is a product of oxidation of the coal.

At normal ground temperatures, the gas drained from bituminous coalbeds is over 90 pct  $\text{CH}_4$  and less than 2 pct higher molecular weight hydrocarbons (table 3). When coal is heated, the rate at which gas is emitted into the atmosphere increases, and the desorption and emission of hydrocarbons other than methane significantly affect the overall emission rate (16). The following represents a hypothetical example of the temperature-dependent emission of hydrocarbons from coal: If a 1-lb lump of coal

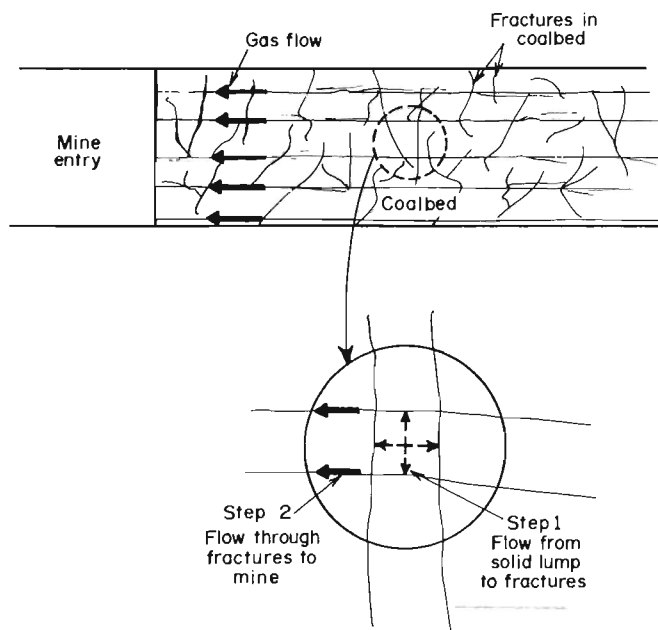


Figure 1.—Two-phase flow of gas from coalbeds (19).

contains 0.01 ft<sup>3</sup> of hydrocarbon gas, it may, at ambient temperature, emit  $1 \times 10^{-5}$  ft<sup>3</sup> of hydrocarbon gas per day. The emitted gas is 98 pct CH<sub>4</sub>. At 125° C, the same lump of coal gives off  $1 \times 10^{-4}$  cfd of hydrocarbon gas, which is less than 50 pct CH<sub>4</sub>. At 150° C, the emission rate is  $2 \times 10^{-4}$  cfd, and the concentration of methane is about 35 pct (fig. 2). In active mines, changes in the emission rate may be related to changes in surface area due to coal breakage or to changes in barometric pressure. In abandoned mines, temperature is the only factor that significantly affects the emission of hydrocarbons from the coal and carbonaceous shale. Since elevated temperatures cause an increase in the concentration of total

hydrocarbons (fig. 3) and a decrease in the relative concentration of methane (fig. 4), a ratio was developed to relate both quantities to a single value. The ratio, R1, is defined as

$$R1 = ((1.01 [\text{THC}] - [\text{CH}_4]) / ([\text{THC}] + C)) \cdot 1,000,$$

where [THC] = total hydrocarbon concentration, ppm,

[CH<sub>4</sub>] = methane concentration, ppm,

and

C = constant, 0.01 ppm.

The ratio R1 was defined to meet the criteria that it would (1) equal zero when and only when the concentration of total hydrocarbons was zero, (2) have a unique value when methane was the only hydrocarbon, (3) eliminate the possibility of division by zero, a consideration in the computer processing of data, and (4) increase as temperature increased. As defined, the ratio R1 is an increasing function of the percentage of higher molecular weight hydrocarbons, has a value of zero when no hydrocarbons are detected, has a value of 10 when methane is the only hydrocarbon, and has a limiting value of about 1,000. In almost all cases, the concentrations of both methane and other hydrocarbons increase as the temperature increases. The extent to which the emission rate increases with temperature is dependent upon factors such as the concentration of methane and other hydrocarbons within the coal, the adsorbate density, the internal surface area, and the relative volumes of the micropores and the macropores. Because of the number of factors that control the emission of hydrocarbons from coal, values of R1 are not correlated to specific temperatures. At a particular temperature, for instance, different coal samples could have significantly different R1 values (fig. 5).

Table 3.—Average composition and heating value of gas from coalbeds

Coalbed	Location	Hydrocarbons, pct					Other gases, pct					Heating value, Btu/scf
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>12</sub>	H <sub>2</sub>	He	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	
Anthracites	PA	98.7	0.1	ND	ND	ND	ND	ND	1.0	ND	0.1	1,053
B Seam	CO	87.8	.05	0.005	0.001	ND	ND	ND	.1	ND	12.0	935
Lower Hartshorne	OK	99.2	.01	ND	ND	ND	ND	ND	.6	0.1	.1	1,056
Mary Lee	AL	96.0	.1	ND	ND	ND	0.001	0.3	3.5	.1	.1	1,022
Pittsburgh	PA, WV	91.1	.3	ND	ND	ND	ND	ND	.5	.2	8.2	975
Pocahontas	VA	94.9	1.3	.004	.002	0.0001	.02	.04	3.2	.2	.3	1,030
Upper Kittanning	PA	97.4	.01	ND	ND	ND	ND	ND	2.3	.2	.1	1,037

ND Not detected.

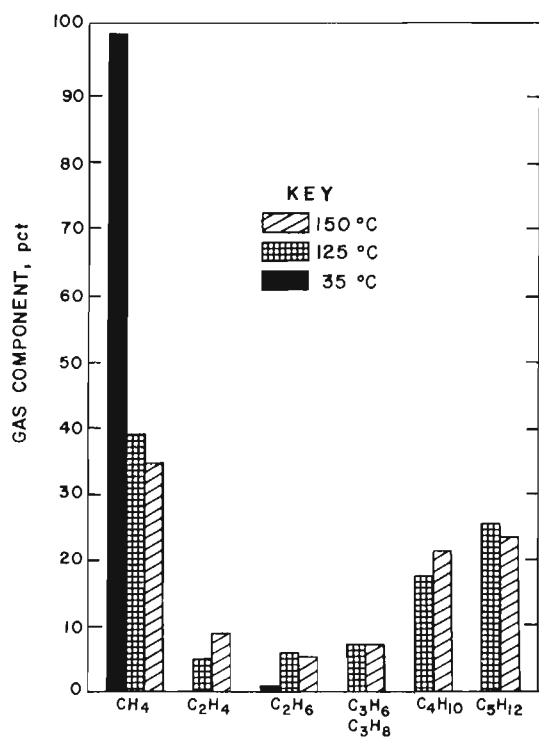


Figure 2.—Relative composition of hydrocarbon gas desorbed from coal with temperature.

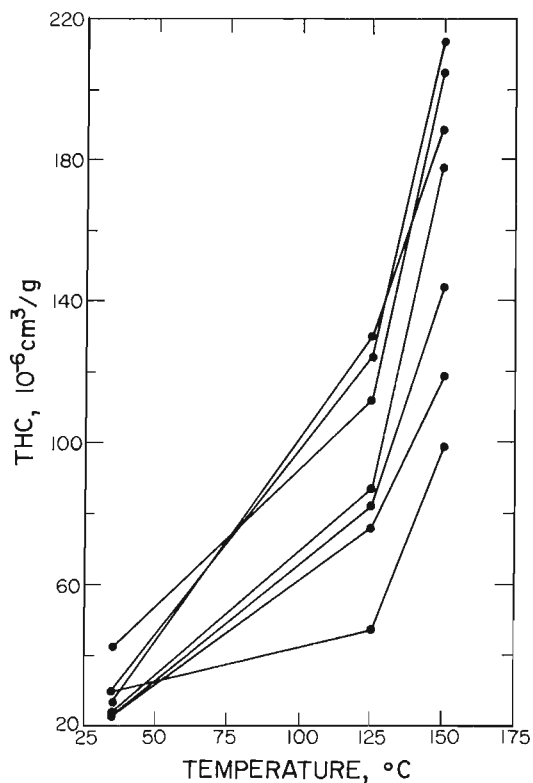


Figure 3.—Variation in emission of total hydrocarbons with temperature.

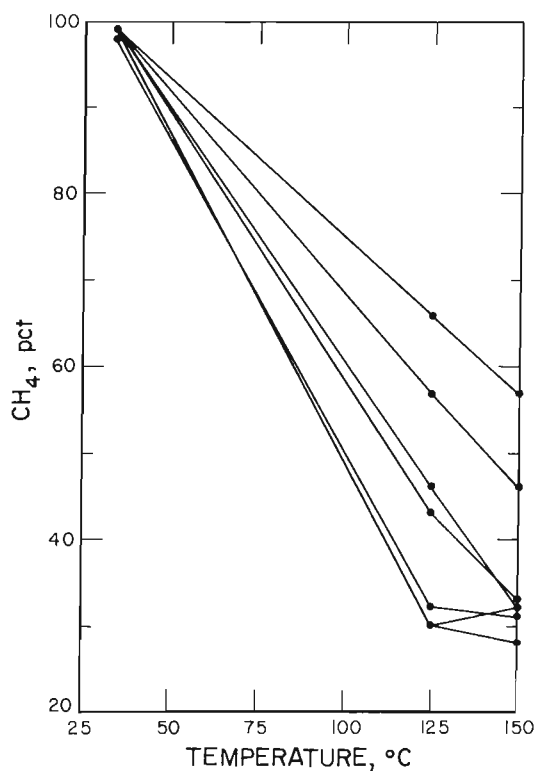


Figure 4.—Percentage of methane in desorbed hydrocarbon gas with temperature.

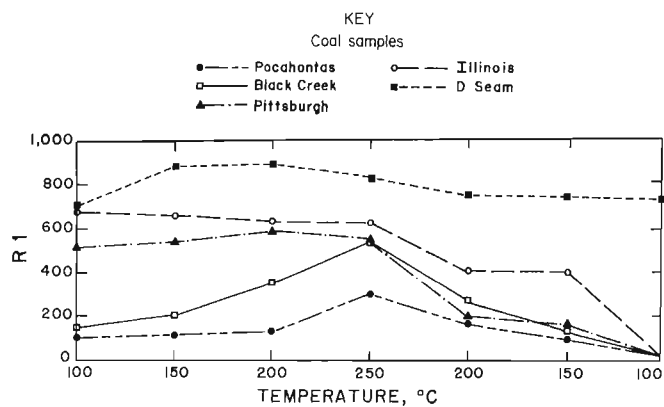


Figure 5.—Typical variations in hydrocarbon ratios with temperature.

The slope of R1 versus temperature will vary with the concentration of total hydrocarbons (fig. 6), again indicating that absolute values of R1 cannot be correlated to specific temperatures. However, elevated values of R1 are related to elevated temperatures, and over a period of time, increasing values of R1 indicate heating and decreasing values of R1 indicate cooling.

The use of a hydrocarbon ratio as a fire signature has several advantages. Hydrocarbon desorption occurs at relatively low temperatures; therefore, the mass of the coal from which the hydrocarbons are desorbed is much larger than that directly affected by combustion. Since the source is larger, the signature is more sensitive. Since a ratio is used, if the concentration is above the detection limit, dilution with air or other combustion products is not a factor. The hydrocarbon ratio is independent of the concentration of other components, such as oxygen and CO<sub>2</sub>, and temperature-dependent desorption is the only mechanism by which hydrocarbons are produced in an abandoned mine. The use of hydrocarbon ratios is a positive and sensitive indicator of remote subsurface combustion.

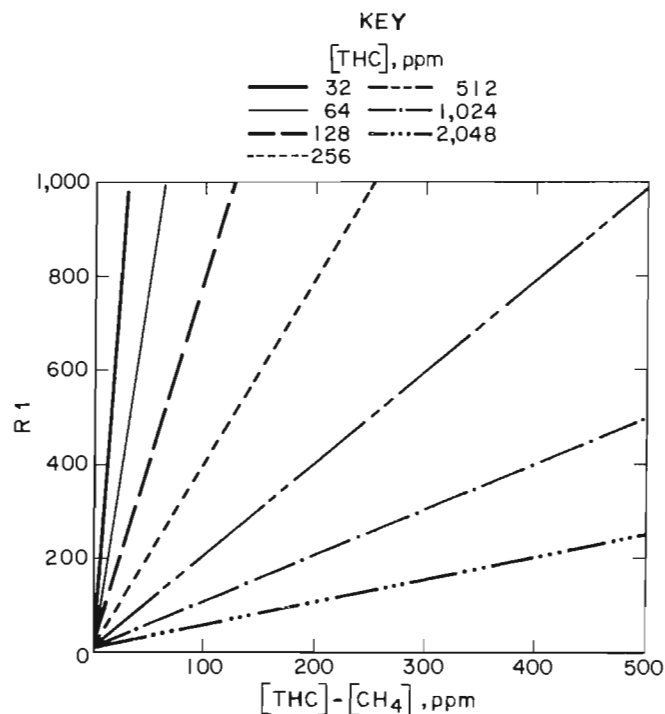


Figure 6.—Effect of total hydrocarbon concentration on increase in hydrocarbon ratio.

## EXPERIMENTAL METHOD

In the laboratory study, an 8-in tubular combustion furnace (fig. 7) was used to heat 11 samples of coal and coal waste (table 4). A 1.5-kg sample was placed in a stainless steel sample boat (fig. 8). Thermocouples and gas-sampling tubes were placed at the air inlet, in the sample boat, and downstream of the furnace (fig. 9). A personal-size sampling pump was used to withdraw samples that were collected in completely evacuated Vacutainer<sup>3</sup> test tubes. Gas samples were analyzed by gas chromatograph for O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, and the C<sub>2</sub> to C<sub>5</sub> hydrocarbons. The hydrocarbons were determined by flame ionization detector with a sensitivity of 1 ppm. Other gases were determined by thermal conductivity detector with a sensitivity of 0.001 pct. With both detectors, the accuracy is considered  $\pm 2$  pct of the amount present.

In the laboratory tests, compressed air at a flow rate of 2 scfh was used initially (table 5). In later tests, a nitrogen-air mixture or nitrogen alone was used to control the tendency of the coal to self-heat. A mixing tank was

used to ensure constant composition of the airstream and to allow the gas to enter the furnace at atmospheric pressure. Reducing the concentration of oxygen had no effect on the desorption of hydrocarbons from the coal samples.

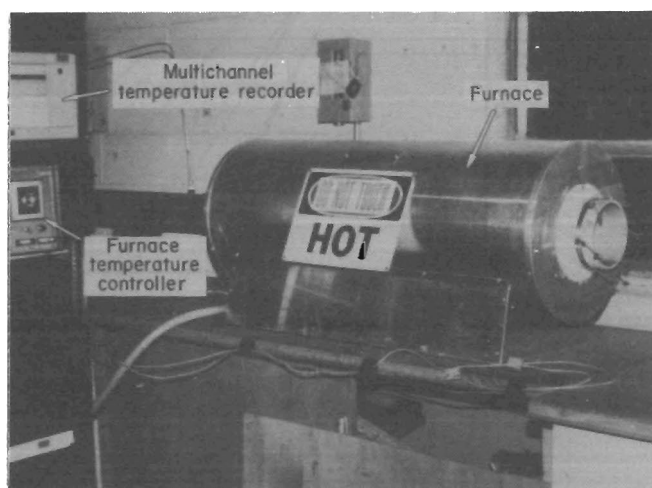


Figure 7.—Combustion furnace.

<sup>3</sup>Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Table 4.—Sample analyses, as received

Sample	Source	Moisture, pct	Ash, pct	VM, pct	FC, pct	Heating value, Btu/lb
Albright waste . . . . .	WV . . . . .	9.1	42.3	17.5	31.2	6,719
Anthracite 1 . . . . .	PA . . . . .	2.3	8.2	7.0	82.6	13,536
Anthracite 2 . . . . .	PA . . . . .	5.0	12.0	4.8	78.1	12,184
Anthracite waste 1 . .	PA . . . . .	1.5	69.6	7.1	21.7	3,492
Anthracite waste 2 . .	PA . . . . .	2.0	60.3	7.0	30.8	4,940
Black Creek . . . . .	AL . . . . .	2.2	2.0	37.2	58.6	14,655
D Seam . . . . .	CO . . . . .	7.9	5.6	36.2	50.3	12,368
Freeport . . . . .	PA . . . . .	1.6	6.1	37.8	54.5	14,196
Illinois No. 6 . . . . .	IL . . . . .	12.0	27.8	29.0	30.7	8,417
Pittsburgh . . . . .	PA . . . . .	1.4	4.8	37.3	56.4	14,205
Pocahontas No. 4 . . .	VA . . . . .	1.0	10.5	16.6	71.9	13,934

FC Fixed carbon. VM Volatile matter.

Table 5.—Experimental parameters

Sample	Test <sup>1</sup>	Heating type	Elapsed time, h	Atmosphere
Albright waste . . . . .	28	C	169	Air, N <sub>2</sub>
	31	C	120	Air, N <sub>2</sub>
	27	I	405	Air, N <sub>2</sub>
Anthracite 1 . . . . .	40	C	52	N <sub>2</sub>
	42	C	53	N <sub>2</sub>
Anthracite 2 . . . . .	46	C	35	N <sub>2</sub>
	47	C	48	N <sub>2</sub>
	49	C	35	N <sub>2</sub> , H <sub>2</sub> O
Anthracite waste 1 . .	41	C	52	N <sub>2</sub>
	43	C	35	N <sub>2</sub>
Anthracite waste 2 . .	51	C	35	N <sub>2</sub>
	53	C	50	N <sub>2</sub>
Black Creek . . . . .	35	C	57	N <sub>2</sub>
	39	C	53	N <sub>2</sub>
	50	C	52	N <sub>2</sub> , H <sub>2</sub> O
D Seam . . . . .	44	C	52	N <sub>2</sub>
	45	C	50	N <sub>2</sub>
Freeport . . . . .	26	C	105	Air, N <sub>2</sub>
	30	C	168	Air, N <sub>2</sub>
	24	I	416	Air, N <sub>2</sub>
	25	I	408	Air, N <sub>2</sub>
Illinois No. 6 . . . . .	36	C	57	N <sub>2</sub>
	37	C	56	N <sub>2</sub>
Pittsburgh . . . . .	23	C	94	Air, N <sub>2</sub>
	29	C	167	Air, N <sub>2</sub>
	21	I	365	Air
	22	I	429	Air
Pocahontas No. 4 . . .	48	C	35	N <sub>2</sub> , H <sub>2</sub> O
	34	C	56	N <sub>2</sub>
	38	C	54	N <sub>2</sub>
	32	C	58	Air, N <sub>2</sub>

C Continuous. I Intermittent.

<sup>1</sup>Test numbers correlate to those used in reference 15.

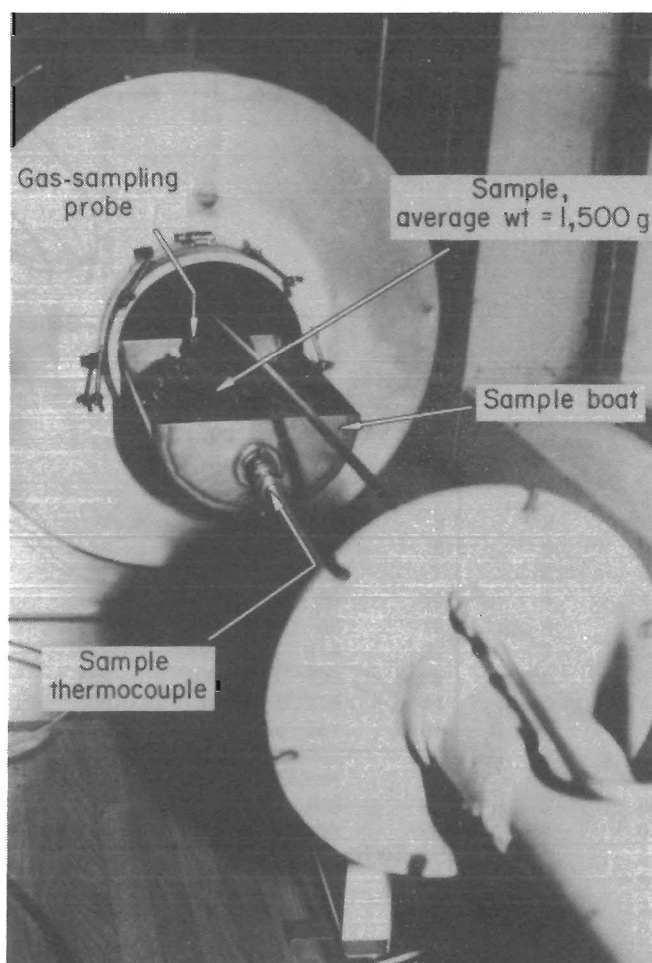


Figure 8.—Combustion furnace with sample and gas-sampling probe.

Two types of temperature regimes were tested (fig. 10). The first type, intermittent heating, was an extended test in which the furnace temperature was raised from ambient to 250° C in 50° C increments. For each increment, the temperature was maintained at that level for approximately 3 days. Each intermittent heating test took approximately 2 weeks to complete. In the second type of test, continuous heating, the temperature controller was set to 250° C and the temperature was allowed to rise

continuously. The furnace temperature was held at 250° C for several hours, and then the furnace was allowed to cool. The continuous heating test took approximately 5 days, and samples were collected during both heating and cooling phases. It was determined that the intermittent (or extended) heating tests produced no more information than the shorter continuous heating tests. Therefore, the discussion of results is based on duplicate continuous heating tests for each sample.

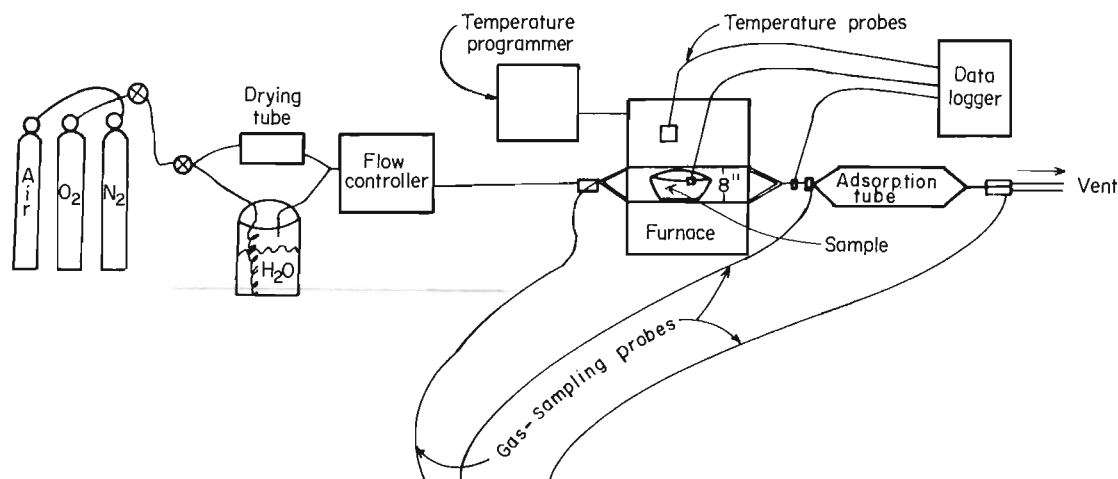


Figure 9.—Schematic of laboratory equipment.

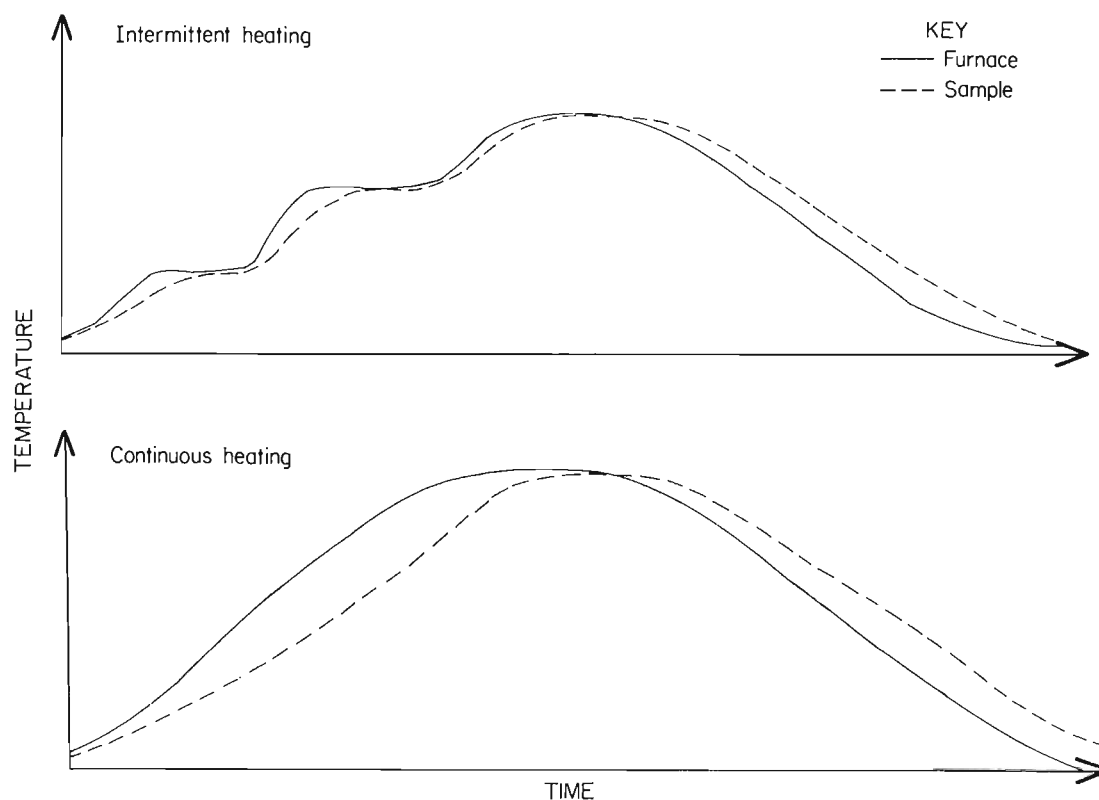


Figure 10.—Experimental temperature regimes.

## RESULTS

Duplicate continuous heating tests were completed on samples of six bituminous coals, one bituminous waste, two anthracite coals, and two anthracite wastes. The results obtained from the continuous heating tests were dependent to some degree upon the rank of the coal. For bituminous samples (Pittsburgh coal, Freeport coal, Albright waste, Pocahontas No. 4 coal, Illinois No. 6 coal, Black Creek coal, and D Seam coal), the concentration of hydrocarbons increased during heating and decreased during cooling (table 6). The concentration of total hydrocarbons for all

bituminous samples, including the waste, was between 100 and 1,000 ppm. The maximum concentration of hydrocarbons from the two anthracite coal samples and one anthracite waste sample was 20 ppm, and the higher molecular weight hydrocarbons were not generally detected. The concentration of total hydrocarbons from the other anthracite waste sample was in the 4- to 90-ppm range, and measurable quantities of higher molecular weight hydrocarbons were desorbed from the sample.

Table 6.—Variation in methane and total hydrocarbon concentrations, in parts per million, with temperature

Sample	Test <sup>1</sup>	Component	Heating					Cooling		
			100° C	150° C	200° C	225° C	250° C	225° C	150° C	100° C
Albright waste . . . . .	28	CH <sub>4</sub>	246	608	603	553	156	8	4	5
		THC	250	626	631	588	192	10	4	5
	31	CH <sub>4</sub>	43	156	153	145	18	10	3	4
		THC	46	160	164	163	30	16	3	4
Anthracite 1 . . . . .	40	CH <sub>4</sub>	4	3	5	6	7	4	2	4
		THC	4	3	5	6	7	4	2	4
	42	CH <sub>4</sub>	3	4	6	7	8	3	2	4
		THC	4	4	7	7	8	3	2	4
Anthracite 2 . . . . .	46	CH <sub>4</sub>	3	4	3	3	6	4	4	3
		THC	3	4	3	3	6	4	4	3
	47	CH <sub>4</sub>	3	3	3	6	7	10	2	3
		THC	3	3	3	6	7	10	2	3
Anthracite waste 1 . .	41	CH <sub>4</sub>	32	65	47	52	31	4	2	4
		THC	36	73	51	57	34	4	2	4
	43	CH <sub>4</sub>	10	41	64	73	78	3	2	4
		THC	12	48	74	83	88	3	2	4
Anthracite waste 2 . .	51	CH <sub>4</sub>	4	8	13	15	16	5	2	2
		THC	4	8	13	15	16	5	2	2
	53	CH <sub>4</sub>	2	4	7	10	14	3	2	2
		THC	2	4	7	10	14	3	2	2
Black Creek . . . . .	35	CH <sub>4</sub>	7	19	35	46	50	5	5	5
		THC	8	29	67	89	107	7	6	5
	39	CH <sub>4</sub>	5	5	16	13	36	10	4	4
		THC	5	6	20	18	67	19	4	4
D Seam . . . . .	44	CH <sub>4</sub>	125	126	142	146	114	33	7	3
		THC	306	542	783	808	683	99	20	5
	45	CH <sub>4</sub>	98	107	100	92	118	44	8	5
		THC	416	662	786	752	561	131	125	6
Freeport . . . . .	26	CH <sub>4</sub>	5,200	8,100	6,300	NA	1,400	10	0	0
		THC	5,248	8,199	6,458	NA	1,584	17	0	0
	30	CH <sub>4</sub>	8,560	6,850	3,780	2,930	269	66	3	0
		THC	8,616	6,924	3,964	3,005	358	66	4	0
Illinois No. 6 . . . . .	36	CH <sub>4</sub>	53	73	84	62	58	17	5	3
		THC	157	198	211	149	133	30	8	3
	37	CH <sub>4</sub>	78	72	85	98	53	13	5	2
		THC	246	208	220	236	126	21	7	2
Pittsburgh . . . . .	23	CH <sub>4</sub>	30	50	65	65	55	10	0	NA
		THC	43	109	152	154	122	17	0	NA
	29	CH <sub>4</sub>	64	84	80	NA	44	17	7	NA
		THC	126	180	163	NA	81	22	8	NA
Pocahontas No. 4 . . .	34	CH <sub>4</sub>	225	261	314	360	215	8	5	5
		THC	243	290	365	396	264	10	5	5
	38	CH <sub>4</sub>	146	296	290	299	109	10	3	2
		THC	163	329	327	352	149	13	3	2
	32	CH <sub>4</sub>	628	1,048	884	776	449	6	8	8
		THC	666	1,127	980	879	566	7	9	8

NA Not available.

<sup>1</sup>Test numbers correlate to those used in reference 15.

In order to simplify the presentation of results, the samples were grouped according to the type of curve obtained when hydrocarbon emission was plotted against temperature. The emission of total hydrocarbons and methane from the 11 samples could be described by 4 emission curve types. The first, type A, was a straight-line type (fig. 11). Emission of total hydrocarbons was low and almost always coincided with the methane emission. The anthracite coal and anthracite waste samples showed this type of emission.

In type B emission, the concentration of both total hydrocarbons and methane increased continuously with temperature, but at different rates (fig. 12). During cooling, the emission rate decreased rapidly for both total hydrocarbons and methane. The Pittsburgh and Black Creek coals exhibited this type of emission.

In type C emission, the concentration of total hydrocarbons increased continuously with temperature; the

concentration of methane increased initially, then leveled off (fig. 13). Emission decreased rapidly during cooling. The Illinois No. 6 and D Seam samples exhibited this type of emission.

In type D emission, total hydrocarbons and methane concentrations increased rapidly with temperature, reaching a maximum concentration at a temperature below 250° C (fig. 14). There was a consistent and relatively small difference between the total hydrocarbons and methane concentrations. Although the concentrations decreased at elevated temperatures, the difference between the concentrations of total hydrocarbons and methane remained consistent. During cooling, the difference in concentrations was less than 10 ppm. The Freeport and Pocahontas No. 4 coals and the Albright waste had type D emission.

Using the total hydrocarbon and methane concentrations, R1 values were calculated for all data points.

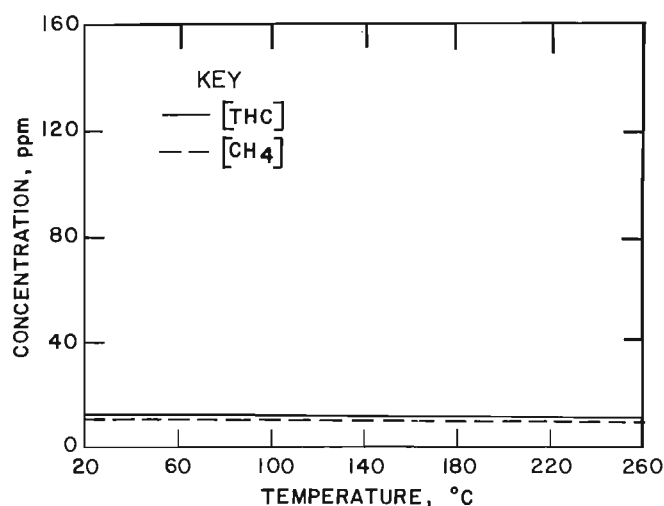


Figure 11.—Type A hydrocarbon emission.

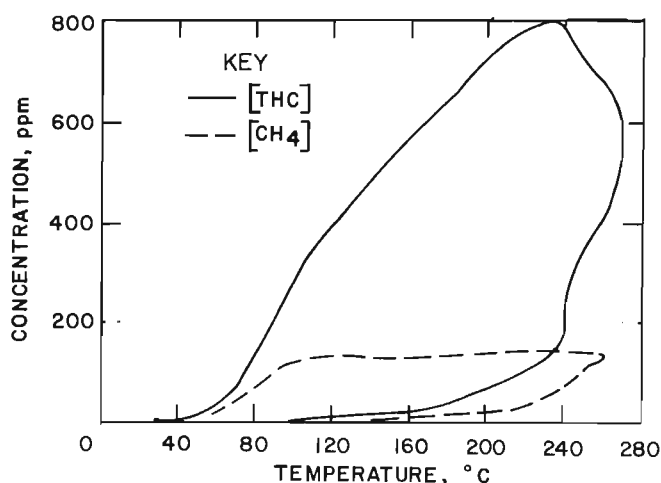


Figure 13.—Type C hydrocarbon emission.

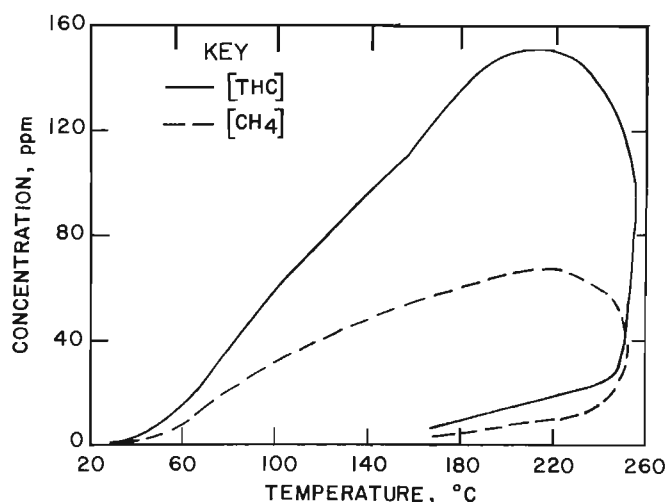


Figure 12.—Type B hydrocarbon emission.

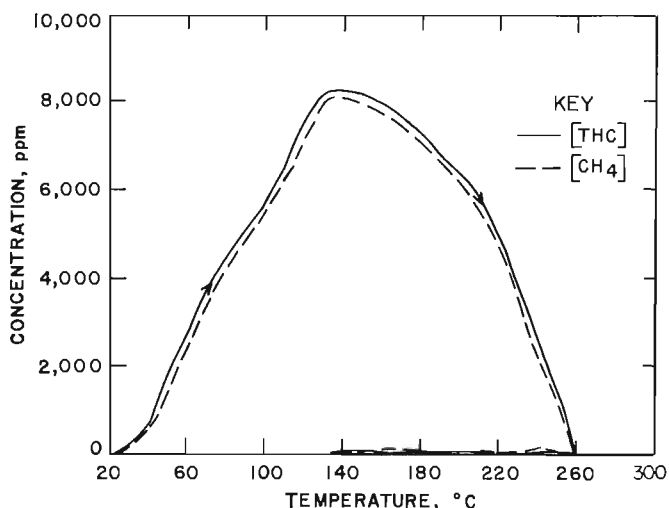


Figure 14.—Type D hydrocarbon emission.



Values within given temperature ranges were then averaged to obtain characteristic values for each sample (table 7).<sup>4</sup> In almost all cases, the value of R1 increased during heating and decreased during cooling. For both anthracite coal samples and one anthracite waste sample, the R1 value was equal to 10 at almost all temperatures. Except for these samples, R1 values during heating were not equal to the R1 values at the same temperature during cooling.

In plotting the hydrocarbon ratios versus temperature, the results fell into three categories. In type I ratios (fig. 15), the value of R1 increased and decreased with temperature. R1 values during heating were higher than those during cooling. Maximum R1 values occurred around 250° C and were in the 600 to 700 range. Those coals with types B and C hydrocarbon emission had type I ratios.

Type II ratios (fig. 16) increased initially at a lower rate than type I ratios. Type II ratios increased rapidly above 200° C and decreased at approximately the same rate during cooling, although the values during cooling could be higher than those during heating. Maximum values of R1 were in the 400 to 600 range. Coals that exhibited type D emission had type II ratios.

Type III ratios were obtained from the anthracite coal and anthracite waste samples. These ratios (fig. 17) showed little variation with temperature, and only one waste sample had R1 values above 100.

The signature characteristics for all the samples are summarized in table 8. The addition of moisture to the gas stream had no significant effect on the R1 values. At temperatures above 100° C, water vapor does not condense

on the coal surface and therefore cannot interfere with the desorption of hydrocarbons.

Although there was no direct correlation between the values of R1 and the elemental or chemical composition of the coal, the characteristic desorption and the ratio types could be correlated with the rank of the coal. Higher rank coals, low-volatile bituminous and anthracite, tend to have a compact physical structure, with an anisotropic fracture system and few well-defined cleavage planes (20-21). The smaller flow channels would limit the mean free path of larger molecules and would tend to depress the desorption and migration of C<sub>2</sub> to C<sub>5</sub> hydrocarbons. Although total hydrocarbon emission rates varied for the different samples of the same coal, the values of R1 tended to be within the same range, indicating that the value of R1 is not dependent on the total amount of gas adsorbed. Although the internal structure of the coal apparently affects the value of R1 at a given temperature, changes in temperature directly cause quantifiable changes in the value of R1 for bituminous coals. These changes can be used to remotely delineate subsurface areas of heated coal.

Limited analysis was performed on possible combustion indicators such as the CO<sub>2</sub>-to-CO ratio, the evolution of CO, or the emission of hydrogen. The use of nitrogen or an air-nitrogen mixture to suppress self-heating of the coal limited the low-temperature oxidation of the samples, thus restricting the production of CO and CO<sub>2</sub>. In general terms, the ratio of CO<sub>2</sub> to CO varied inversely with temperature to a limiting value of 3 (fig. 18) and seemed to be independent of the concentration of oxygen in the airstream. The emission of hydrogen from coal requires the breaking of carbon hydrogen bonds. At the temperatures in this study (less than 250° C), there was insufficient energy to break bonds, and the emission of hydrogen from the heated coal was generally insignificant.

<sup>4</sup>R1 values calculated from data in table 6 may not agree with those listed in table 7 because of the independent averaging program used and because of rounding.

Table 7.—Variation in average hydrocarbon ratio with temperature

Sample	Heating					Cooling			
	100° C	150° C	200° C	225° C	250° C	225° C	200° C	150° C	100° C
Albright waste . . . . .	50	30	40	50	75	400	125	60	30
Anthracite 1 . . . . .	130	10	80	10	10	10	10	10	10
Anthracite 2 . . . . .	10	10	10	10	10	10	10	10	10
Anthracite waste 1 . .	150	145	140	125	115	115	10	10	10
Anthracite waste 2 . .	10	10	10	10	10	10	10	10	10
Black Creek . . . . .	150	200	350	440	540	400	250	125	10
D Seam . . . . .	710	880	890	910	825	700	625	690	675
Freeport . . . . .	20	50	70	80	150	325	275	225	10
Illinois No. 6 . . . . .	675	660	625	625	625	410	375	375	10
Pittsburgh . . . . .	405	520	540	590	550	550	200	180	150
Pocahontas No. 4 . . .	90	100	110	125	150	300	190	160	85

Table 8.—Summary of signature characteristics of coal and waste samples

Sample	Test <sup>1</sup>	Emission type <sup>2</sup>	[THC] <sub>max</sub> <sup>3</sup> ppm	T1, <sup>4</sup> °C	R1 <sub>max</sub> <sup>5</sup>	T <sub>R1</sub> , <sup>6</sup> °C
TYPE I RATIO						
Black Creek . . . . .	35	B	100	65	548	263
	39	B	90	40	504	240
	50	B	335	100	520	228
D Seam . . . . .	44	C	800	40	880	233
	45	C	830	40	890	231
Illinois No. 6 . . . . .	36	C	225	40	680	100
	37	C	275	40	621	245
Pittsburgh . . . . .	23	B	500	60	586	242
	29	B	150	60	531	270
	48	B	500	150	670	265
TYPE II RATIO						
Albright waste . . . . .	28	D	600	200	367	238
	31	D	165	100	477	257
Freeport . . . . .	26	D	8,200	240	360	255
	30	D	8,900	230	541	258
Pocahontas No. 4 . . .	34	D	400	100	403	264
	38	D	400	60	340	255
TYPE III RATIO						
Anthracite 1 . . . . .	40	A	10	NAp	10	NAp
	42	A	10	NAp	10	NAp
Anthracite 2 . . . . .	46	A	10	NAp	10	NAp
	47	A	10	NAp	10	NAp
Anthracite waste 1 . .	49	A	14	NAp	10	NAp
	41	A	80	90	125	130
Anthracite waste 2 . .	43	A	90	80	176	242
	51	A	20	NAp	10	NAp
	52	A	15	NAp	10	NAp

NAp Not applicable.

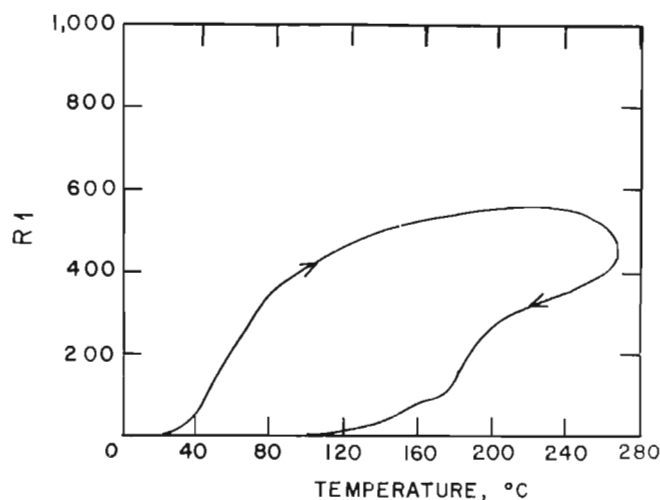
<sup>1</sup>Test numbers correlate to those used in reference 15.<sup>2</sup>Emission types are shown in figures 11-14.<sup>3</sup>Maximum concentration of hydrocarbons in any 1 sample.<sup>4</sup>Temperature at which R1 exceeds 100.<sup>5</sup>Maximum value of R1.<sup>6</sup>Temperature at which maximum value of R1 occurs.

Figure 15.—Type I hydrocarbon ratio.

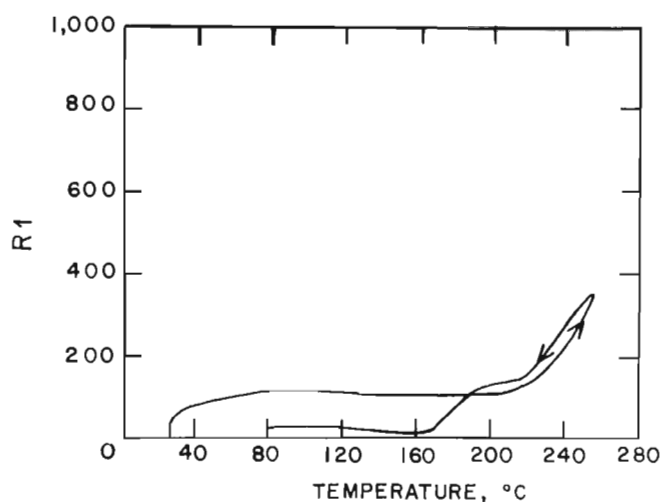


Figure 16.—Type II hydrocarbon ratio.

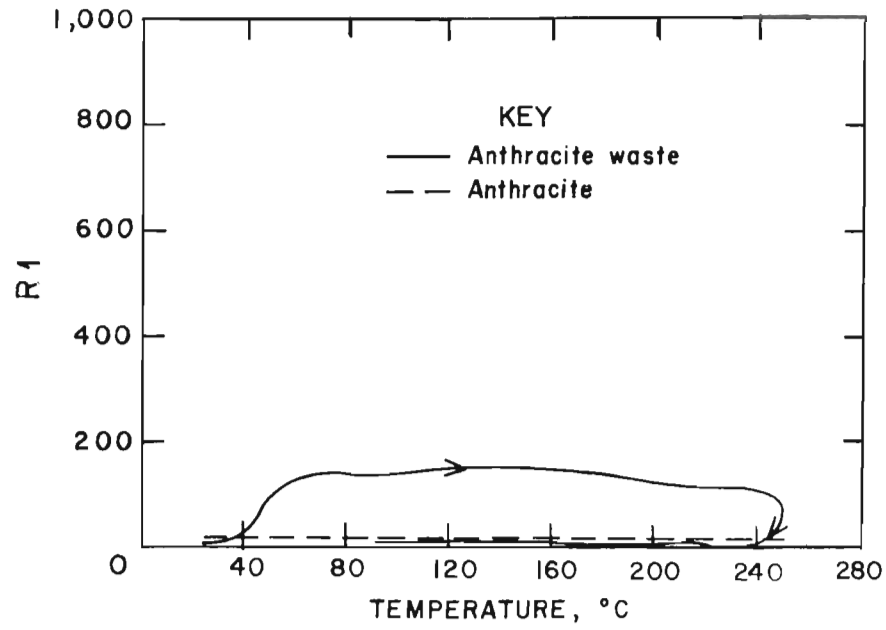


Figure 17.—Type III hydrocarbon ratio.

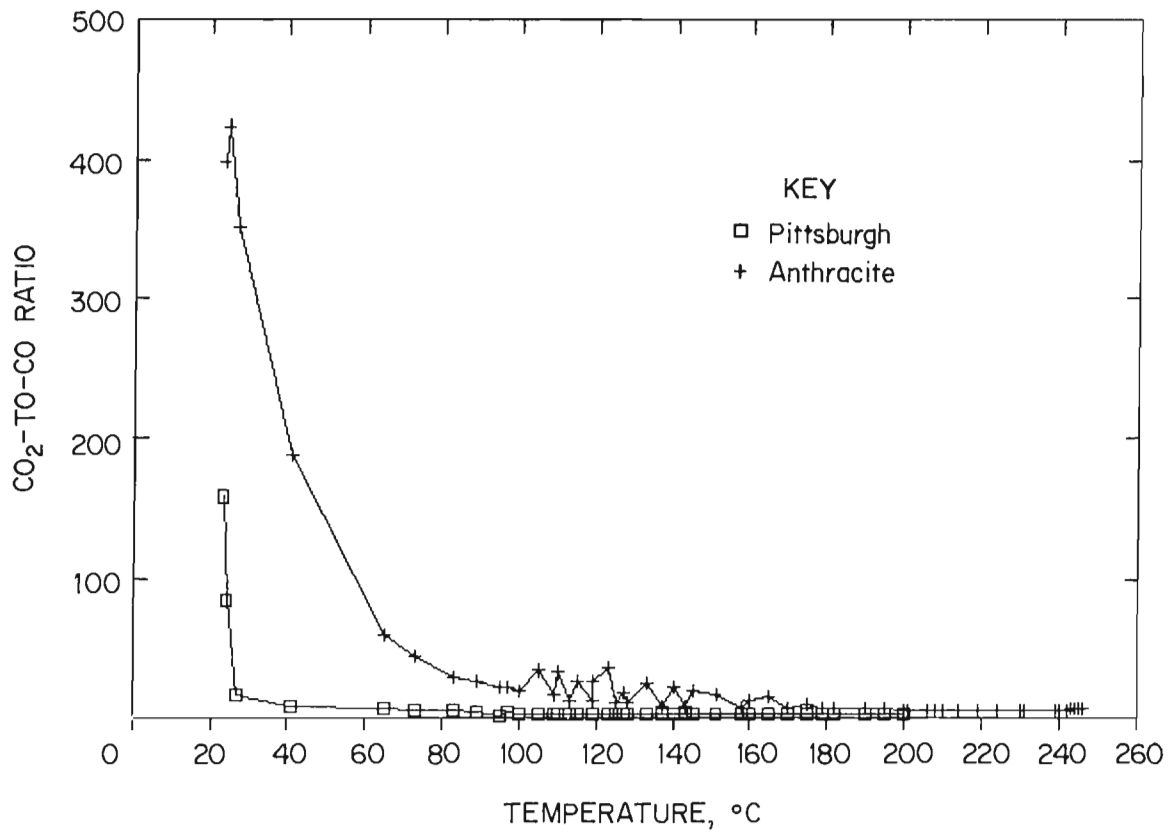


Figure 18.—Variation in CO<sub>2</sub>-to-CO ratio with temperature.

## FIELD EXPERIENCE

To apply this concept to the location and monitoring of remote combustion, a mine fire diagnostic methodology is being developed that incorporates the use of the hydrocarbon ratio and borehole communication testing (11). This mine fire diagnostic method compares measured values of temperature and pressure at the bottom of boreholes in a network under natural or baseline conditions and when an induced draft or exhaust fan is used to impose a pressure gradient (fig. 19). Changes in pressure establish the degree of communication between the sampling point (borehole) and the suction point (fan). It is assumed that mine gases flow radially from the surrounding underground areas toward the point at which the suction is applied. Differences in the hydrocarbon ratio at the

sampling points can be related to the movement of combustion products in assumed directions from the source toward the suction point. In a simplified depiction of this concept, shown in fig. 20, the exhaust fan is attached to the leftmost hole. If there is communication between the exhaust hole and the neighboring holes, a decrease in static pressure will be measured at the bottom of each casing. If a fire exists to the right of the rightmost hole (case A), combustion products will be detected in gas samples taken at each borehole. Similarly, a heating between the exhaust hole and its nearest neighbor (case C), would be detected only at the exhaust hole. To verify the location of heating, the fan is moved to another borehole and the communication test is repeated.

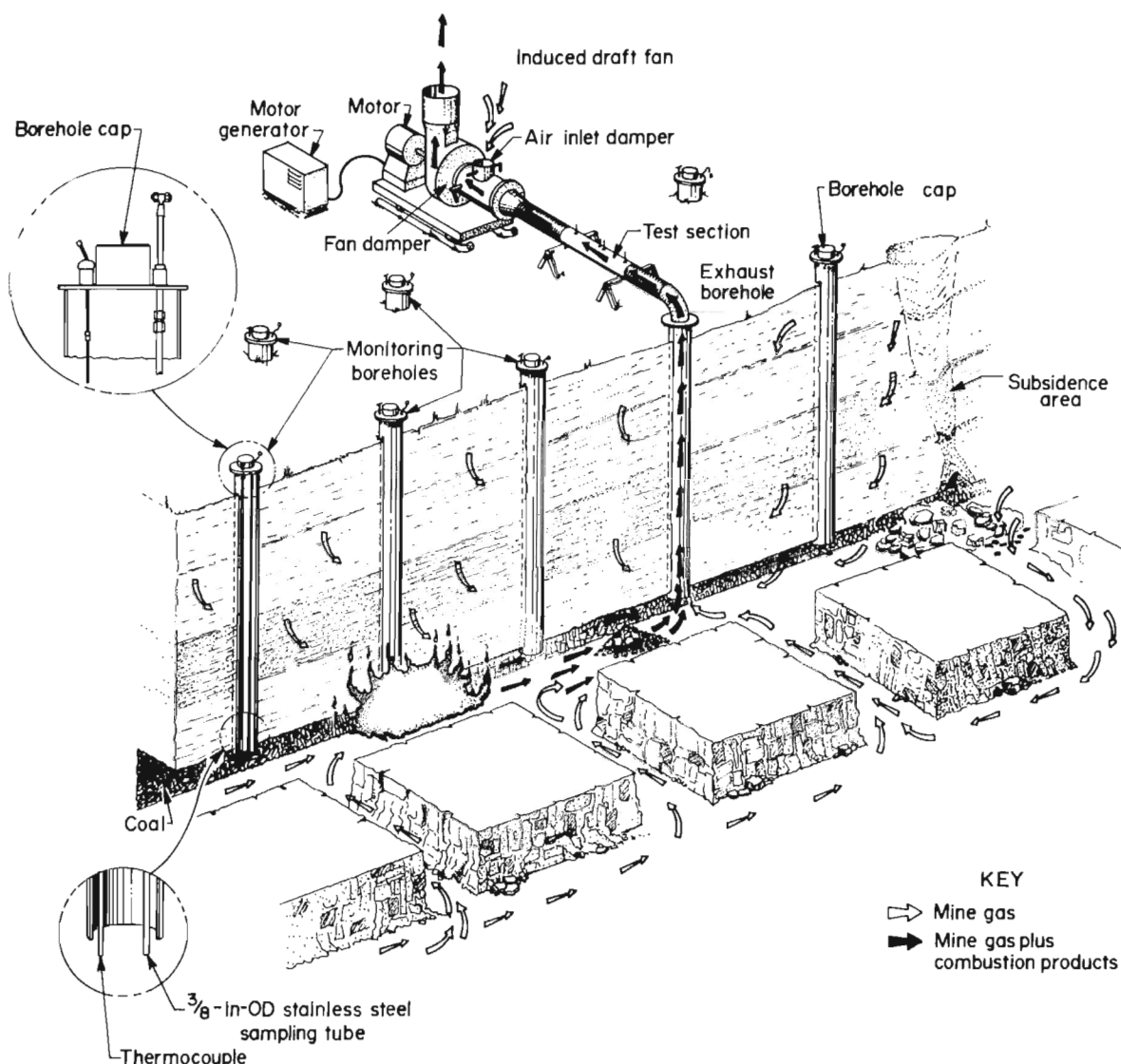


Figure 19.—Mine fire diagnostics: communication testing.

The mine fire diagnostic method has several advantages: (1) changes in hydrocarbon emission are caused only by changes in temperature, (2) changes in hydrocarbon emission can be detected for temperatures below the ignition point of coal, increasing the effective amount of coal that serves as a source, (3) hydrocarbons can be detected at concentrations as low as 1 ppm, (4) the use of an appropriate ratio can eliminate the effects of sample dilution, (5) induced pressure effects can be detected as much as several hundred feet from the suction point, and (6) operation is fairly simple, requiring only readily available equipment and normal technical skills.

Hydrocarbon ratios have been or are being used, in conjunction with borehole communication testing, to locate and/or monitor fires in abandoned mines in three locations. At the Renton Mine Fire Extinguishment Project in northern Allegheny County, PA, water injection-fume exhaustion was used in an attempt to extinguish a fire in an abandoned underground coal mine in the Pittsburgh Seam (6). Mine fire diagnostics were used in locating combustion zones and in monitoring the progress of the fire extinguishment effort. Localized venting had been observed at several locations in the 30-acre site. Aerial infrared survey, surface inspection, and borehole temperature monitoring had been unable to locate the source of fumes and vapors emitted from fractures and vents. Borehole communication testing was used with the determination of hydrocarbon emission and CO<sub>2</sub> and CO concentrations. The CO<sub>2</sub>-to-CO ratio results were ambiguous, but the hydrocarbon values indicated the presence of three noncontiguous combustion areas. The total area affected by combustion was determined to be less than 10 acres. During the effort to extinguish the fire, hydrocarbon ratios were correlated to increasing or decreasing subsurface combustion activity (fig. 21). Time-dependent monitoring of the hydrocarbons indicated that the fire extinguishment method did not cause a consistent and

continued decrease in combustion activity at all three of the Renton subsites.

At Large, PA, a fire in an abandoned underground mine is located at the base of a steep hill. A natural gas pumping station is located on the top of the hill, and high-pressure gas transmission pipes and high-voltage electric transmission lines cross the site. Because of the terrain and the utilities on the surface, it was considered essential to determine the exact location of the combustion areas. Mine fire diagnostic testing, utilizing six 6-in and thirty-one 8-in boreholes on approximately 100-ft centers, indicated an inverted-L-shaped combustion zone (fig. 22). The base of the L was near the outcrop (boreholes 15, 34, 44, and 45); the leg of the L (boreholes 16, 20, and 42) extended into the abandoned mine, probably along a set of main entries. A small isolated combustion zone (borehole 6) was located several hundred feet from the primary combustion area. Areas in which hydrocarbon combustion signatures could not be detected coincided with areas of high water influx, indicating that surface moisture could be preventing the desorption of hydrocarbons from the coal.

At Carbondale, PA, in the Northern Anthracite Field, surface smoke and snow melt indicated continuing combustion at the site of a previous fire control effort. Since surface structures had been built over what was assumed to be an extinguished fire, the mine fire diagnostic method was used to determine the subsurface proximity of combustion to the buildings. Carbondale is considered to be a worst case scenario for the mine fire diagnostic technology. The boreholes that were at the site were cased to 6-in ID, meaning that most of the available

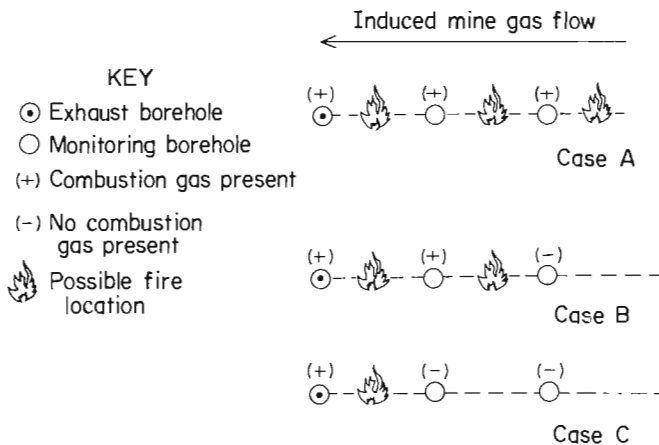


Figure 20.—Schematic of communication testing.

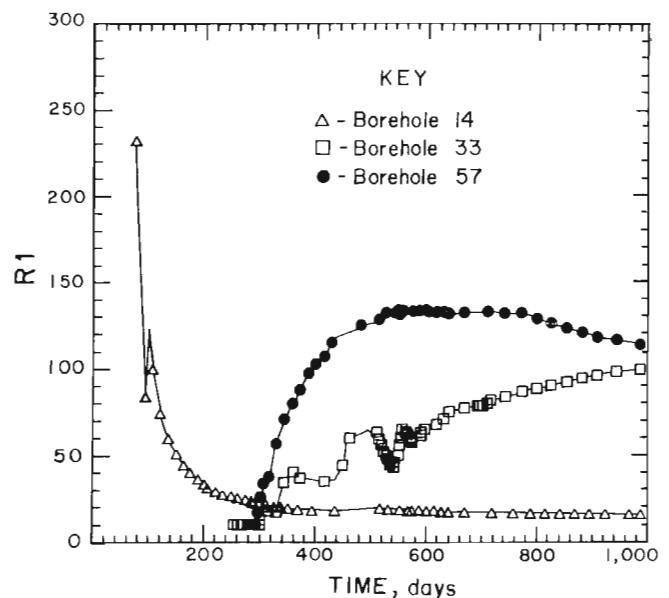


Figure 21.—Time-dependent monitoring of Renton mine fire. (Borehole numbers are those used in the original study (6).)

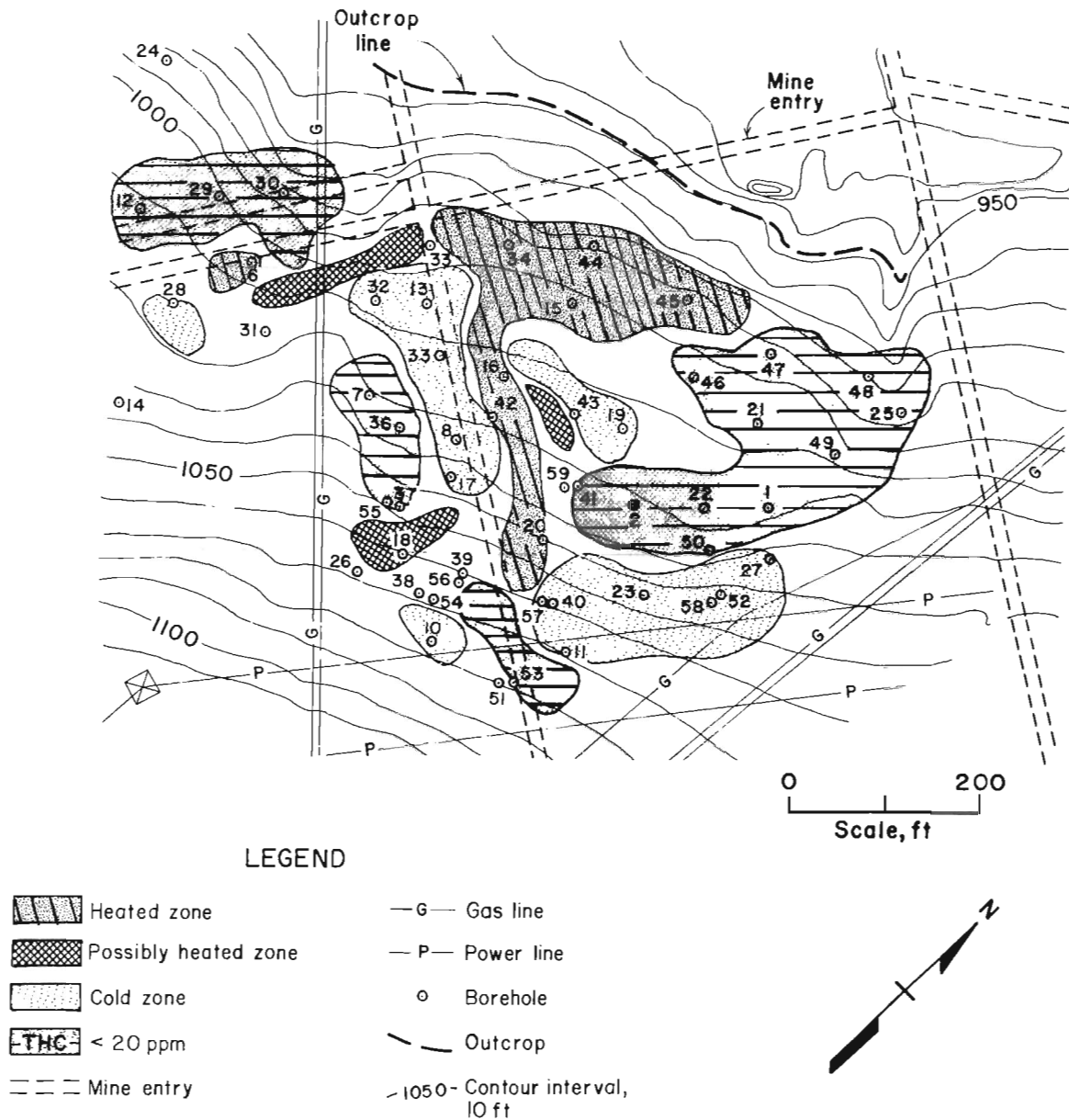


Figure 22.—Large, PA, mine fire site. Heated zones were estimated using Bureau hydrocarbon ratio and Venn diagram technique. (Borehole numbers are those used in the original study (17).)

horsepower would be used to lift air from the bottom to the top of the exhaust borehole, limiting the ability to impose a pressure gradient underground. In several cases, the casing extended through the coal seam, limiting access to the potential combustion zone. The coal was anthracite, which has a relatively low hydrocarbon emission rate, and a fault crossed the property, which could affect the normal

movement of mine gases underground. Despite the non-ideal conditions, the test at Carbondale was successful in locating subsurface areas affected by combustion (fig. 23). Two induced draft fans, connected in series, were used to provide sufficient pressure gradient, and the concentration of methane was used as the combustion indicator.

The presence of hydrocarbon gases does not directly indicate the presence of combustion. Hydrocarbon gases are desorbed from coal at temperatures between 50° and 300° C, which are below the combustion temperature for coal. The presence of these gases indicates that coal in the area has been heated to temperatures higher than ambient. Coal within the heated zone has been affected by combustion, and within that area, a much smaller

volume of coal is the fuel for smoldering combustion. It is not unusual to detect isolated areas (boreholes 17, 32, 33, and 38) in which combustion signatures are found in only one direction. In effect, the mine fire diagnostic method detects cold zones (those not affected by combustion) and limits the area in which combustion activity can be inferred.

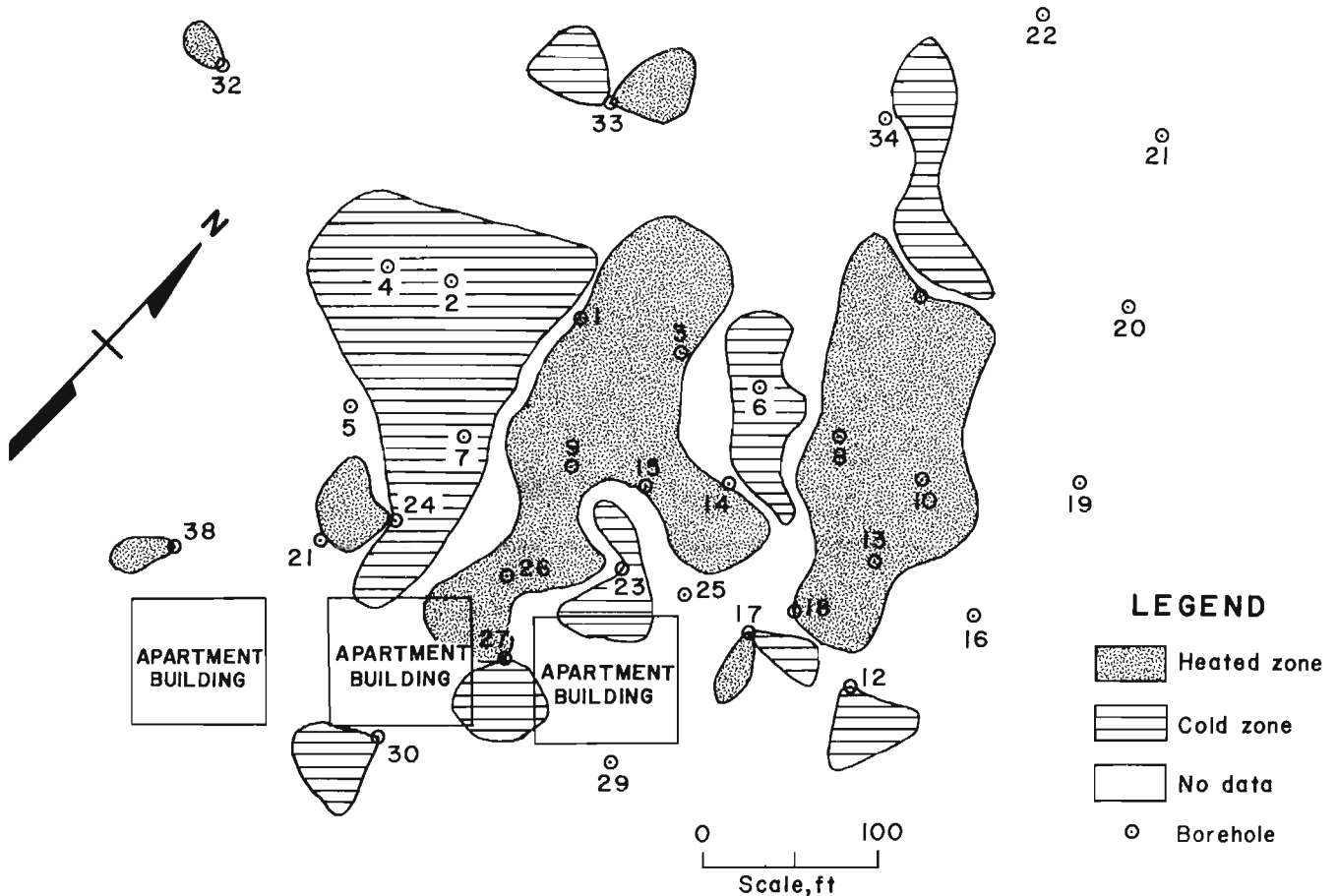


Figure 23.—Carbondale mine fire site. (Borehole numbers are those used in the original study (11).)

## CONCLUSIONS

The laboratory determination of signature criteria measured temperature-induced variations in a ratio based on the concentration of hydrocarbon gases desorbed from coal. For purposes of ease of calculation and presentation, the ratio was defined as

$$R1 = ((1.01 [\text{THC}] - [\text{CH}_4])/([\text{THC}] + 0.01)) \cdot 1,000.$$

When no hydrocarbons are detected, the ratio is zero; when methane is the only hydrocarbon, the ratio is 10. Values above 10 indicate an increased concentration of higher molecular weight hydrocarbons and, therefore, higher temperatures. For all of the bituminous samples studied, values of R1 increased with increasing temperature and decreased during cooling. Because of variations in the gas content of the samples and differences in the internal structure of the coal, values of R1 did not correspond to a unique temperature. However, changes in the value of R1 can be used to infer the location of sub-surface heated and cold zones. Time-dependent changes in R1 can also be used to monitor changes in the extent of

combustion zones, particularly during fire extinguishment efforts.

The ratio R1 was not as applicable to anthracite samples because of the lower rate of hydrocarbon emission and the very low concentration of higher molecular weight hydrocarbons. Changes in the concentration of methane were used in a field study to indicate the presence of heated anthracite.

The laboratory determination of hydrocarbon emission ratios, particularly for bituminous samples, indicates that such ratios are strongly temperature dependent. The relative ease with which the necessary gas samples can be obtained and the available analytical methodology simplify the development of a routine field technique. Manipulation and presentation of the mass of data generated during a field test require further work for maximum efficiency. But the results of the laboratory work, as well as field experience, indicate that signature criteria based on hydrocarbon ratios are a significant improvement in attempts to locate and monitor fires in abandoned underground mines.

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